Li-Ion Battery Anodes from Electrospun Nanoparticle/Conducting Polymer Nanofibers

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Project ID ES264

Overview

Timeline

- October 1, 2016
- September 30, 2018
- Percent complete: 20%

Budget

- Total project funding
  - DOE $1,040,000
  - Contractor $117,062 (VU)
- Funding received in FY 2015: $91,365
- Funding for FY 2016: $330,000

Barriers

- Barriers addressed
  - Capacity fade when using Si as the anode material in a Li-ion battery
  - Achieving high volumetric, gravimetric, and areal energy densities at moderate C-rates
- Targets
  - Gravimetric capacity: 1,200 mAh/g (0.1C)
  - Areal capacity: 3 mAh/cm^2 (0.1C)
  - Volumetric capacity: 800 mAh/cm^3 (0.1C)
  - 40% capacity retention at 2C

Partners

- Lawrence Berkeley National Lab
- Oak Ridge National Lab
- e-Spin Technologies, Inc.
- Project Lead: Peter N. Pintauro, Vanderbilt University

Project Relevance and Objectives

Project Objectives:

To fabricate and characterize nanofiber anode mats containing Si nanoparticles and an electronically conductive binder for Li-ion batteries, where the mats exhibit:

- A gravimetric capacity above 750 mAh/g after 50 cycles at 0.1C
- An areal capacity of 3 mAh/cm^2 after 50 cycles at 0.1C
- A volumetric capacity near 800 mAh/cm^3 after 50 cycles 0.1C
- Exhibit high energy density with minimal capacity fade up to 2C

2015-2016 Project Goals:

1. Synthesize one conductive binder of sufficient quantity and purity for electrospinning.
2. Identify solution composition and electrospinning conditions necessary to electrospin nanofiber mats containing at least 50% Si nanoparticles and conductive binder.
3. Carry out a preliminary evaluation of the electrochemical performance of Si-based nanofiber anodes in a Li-ion battery half cell.
4. Develop a second conductive polymer binder for electrospinning studies in 2017

Milestones

Month/Year	Milestone or Go/No-Go Decision	Status
December 2015	Milestone: Demonstrate at least one conductive binder ready for electrospinning in sufficient quantity and purity.	Complete.
March 2016	Milestone: Demonstrate at least one successfully electrospun composite anode containing at least 50% Si and/or SiO and one conductive polymer binder particles.	Complete
June 2016	Milestone: Demonstrate a coin cell anode discharge capacity above 500 mAh/g after 10 cycles at 0.1C rate.	Complete
September 2016	Go/No-Go Decision: Demonstrate an initial capacity above 500 mAh/g and 90% capacity retention after 50 cycles at 0.1C rate.	On track
December 2016	Milestone: Demonstrate that at least one new conductive binder has been synthesized and is ready in sufficient quantity for electrospinning.	On track

Overall Approach

We will fabricate and characterize Li-Ion battery anodes with:

1. High Li capacity Si nanoparticles
2. New electrochemically stable electronically conductive polymer binders
3. Particle/binder nanofiber mat anode morphology that allows for electrolyte intrusion and short Li^+ ion transport pathways

Our approach addresses the problems with conventional Si anodes

- Our conductive binder will minimize Si particle electrical isolation due to expansion/contraction during cycling.
- Intra- and interfiber porosity of nanofiber mats will allow for the use of thicker anodes with higher areal and volumetric capacities due to electrolyte penetration throughout the electrode.
- Anode porosity and short Li^+ transport pathways in a fiber mat anode will allow for good performance at high C-rates.

Technical Accomplishments and Progress

1. An electronically conductive polymer binder (PFM) was synthesized by G. Liu at LBNL and electrospun into fibers at Vanderbilt University.

   1 wt% poly(ethylene oxide) (PEO) carrier polymer was required for electrospinning uniform fibers. The average fiber diameter of the PFM/PEO fibers was ~1.5 μm. Milestone M1 was achieved.

2. 20-50 wt% Si nanoparticles were incorporated into electrospun PFM/PEO fibers.

   Electrospinning at 15% RH resulted in a dense fiber structure while spinning at 75% RH formed ~100 nm pores on the fiber surface. The diameter of the Si/PFM/PEO fibers ranged from ~1.5 – 9 μm. Milestone M2 was achieved.

3. Nanofiber mats containing Si nanoparticles, carbon black, and poly(acrylic acid) (PAA) were prepared using electrospinning. Baseline performance data were collected for the Si/C/PAA nanofiber mat anodes.

   Compacted and welded Si/C/PAA nanofiber anodes exhibited high gravimetric (1,000 mAh/g), areal (3.5 mAh/cm^2), and volumetric capacities (560 mAh/cm^3). The Si/C/PAA nanofiber anodes were stable over 30 cycles with minimal capacity fade (Milestone M3 was achieved).

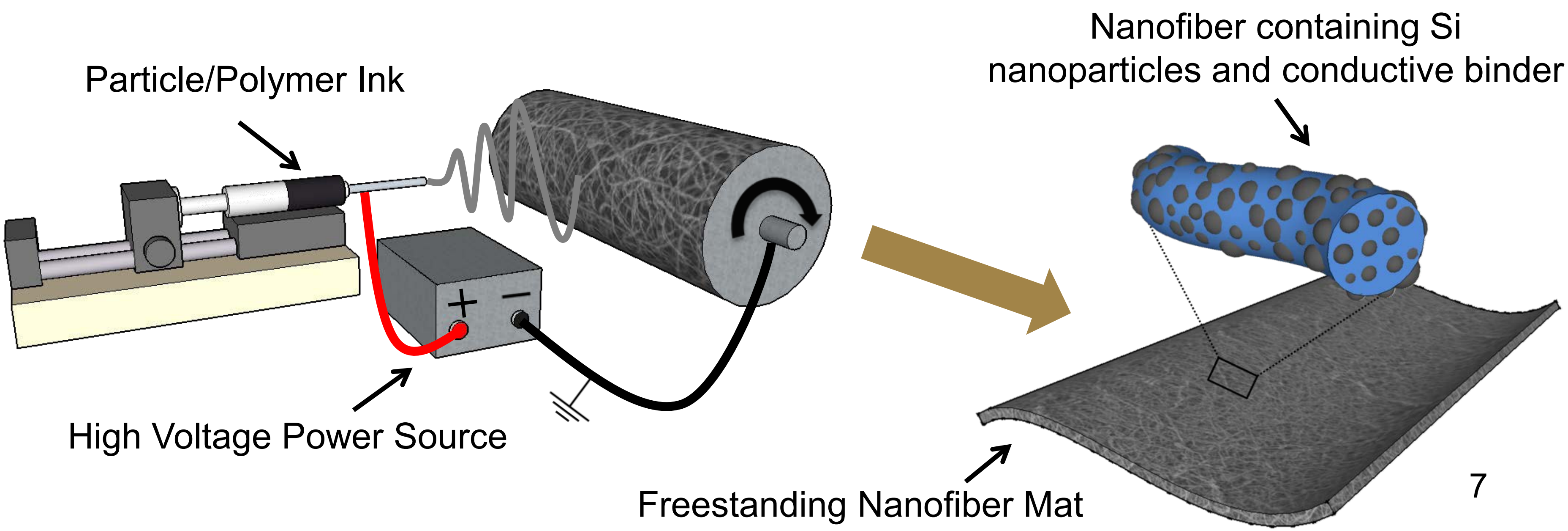
Particle/Polymer Electrospinning

Electrospun nanofiber anodes:

- Si nanoparticles with conductive polymer binder from G. Liu at LBNL
- Si nanoparticles with carbon powder and poly(acrylic acid)

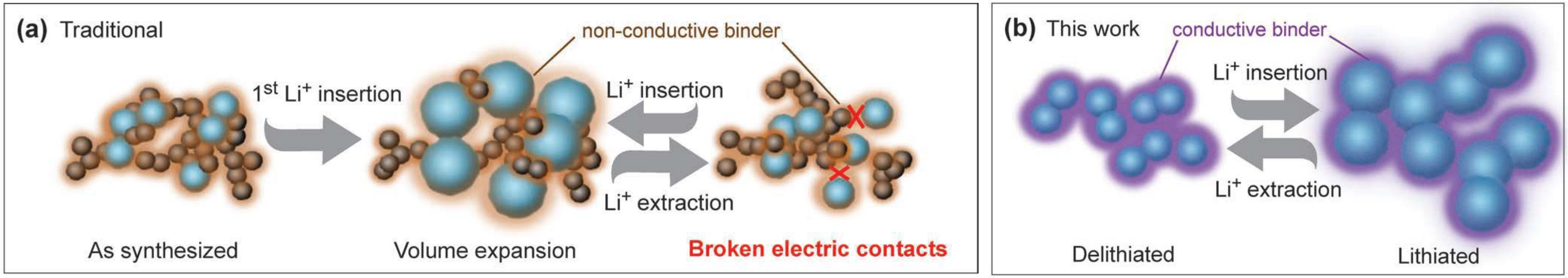
Advantages of a Nanofiber Mat Anode:

- High surface area/volume ratio
- Short Li^+ transport pathways
- Controllable fiber volume fraction (for high volumetric capacity)
- Utilize thick electrodes (for high areal capacity)
- Method is robust and can accommodate different Si sizes and binder formulations



New Electrically Conductive Binders

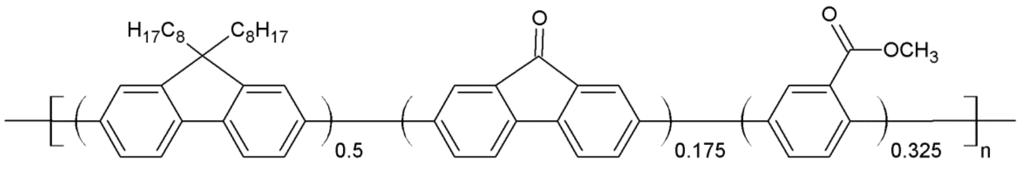
Use conductive binders that adheres of Si surface to prevent electrical isolation of Si particles during charge/discharge cycling.



Images from G. Liu et al., *Adv. Mater.* **2011**, *23*, 4679-4683.

Polymer from Gao Liu, LBNL:

Poly(9,9-dioctylfluorene-co-**f**luorenone-co-**m**ethylbenzoic ester)



P **F** **M**

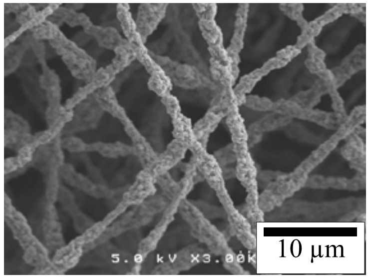
PFM Binder Properties[1,2]

- Mn ~ 20,000 Da
- Electrical Conductivity ~ 1x10^{-5} S/cm
- Swelling in Battery Electrolyte ~ 10 wt%

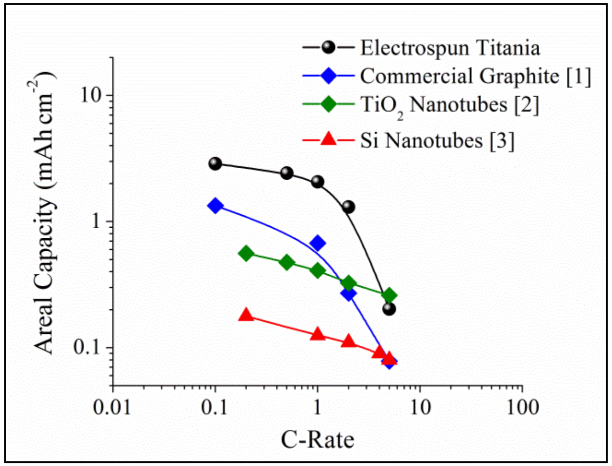
[1] G. Liu et al., *Adv. Mater.* **2011,** 23, (40), 4679-83.
[2] M. Wu et al. *J. Am. Chem. Soc.* **2013,** 135, (32), 12048-56.

Previous Work on Electrospun Anodes Showing the Importance of Fiber Mat Morphology

Titania-based Fiber Mat Anodes



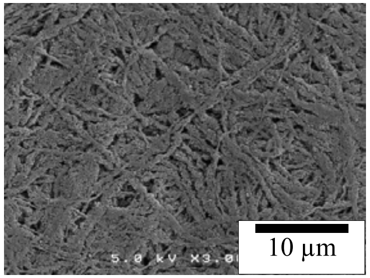
- 40% TiO_2 nanoparticles
- 25% carbon black
- 35% poly(acrylic acid)



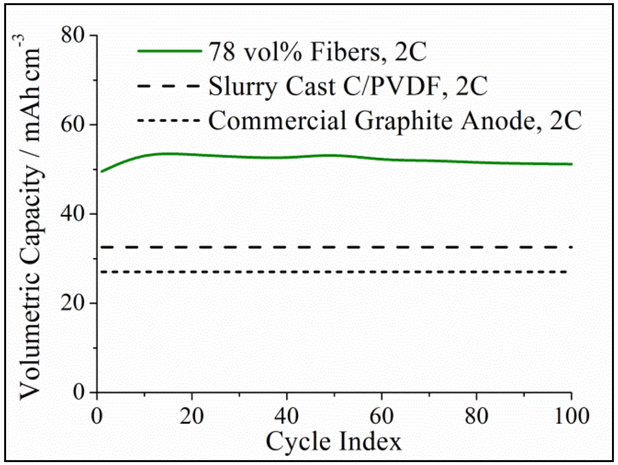
1mm thick titania anodes were prepared for high areal capacity. Fiber mat porosity allows for good performance at high C-rates

[1] S.R. Sivakkumar et al. *Electrochim. Acta* **2010**, *55,* 3330-3335.
[2] W. Wei et al. *J. Mater. Chem. A* **2013**, *1*, 8160-8169.
[3] H. Wu et al. *Nat. Nanotechnol.*, **2012**, *7*, 310-315.

Carbon Nanofiber Mat Anodes



- 65% carbon nanoparticles
- 35% poly(vinylidene fluoride) (PVDF)
- Compact mats to 80 vol% fibers



Carbon nanofiber mats containing 80 vol% fibers exhibit a 2-fold higher volumetric capacity at 2C,as compared to conventional slurry cast materials.

Titania Fiber Anodes: E. C. Self et al. *J. Power Sources* **2015**, *282*, 187-193.
Carbon Nanofiber Anodes: E. C. Self et al., *ChemSusChem* **2016**, *9*, 208-215.

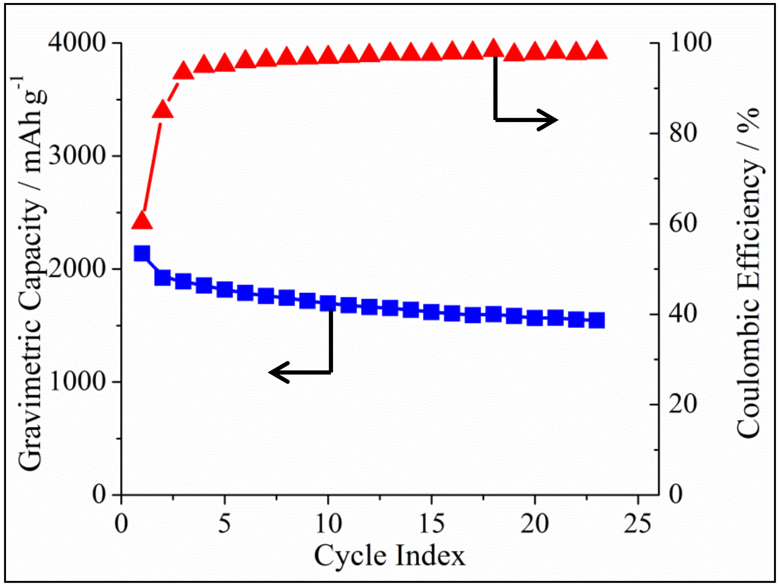
Preliminary Slurry Cast Anodes at Vanderbilt with Si Powder and PFM Binder

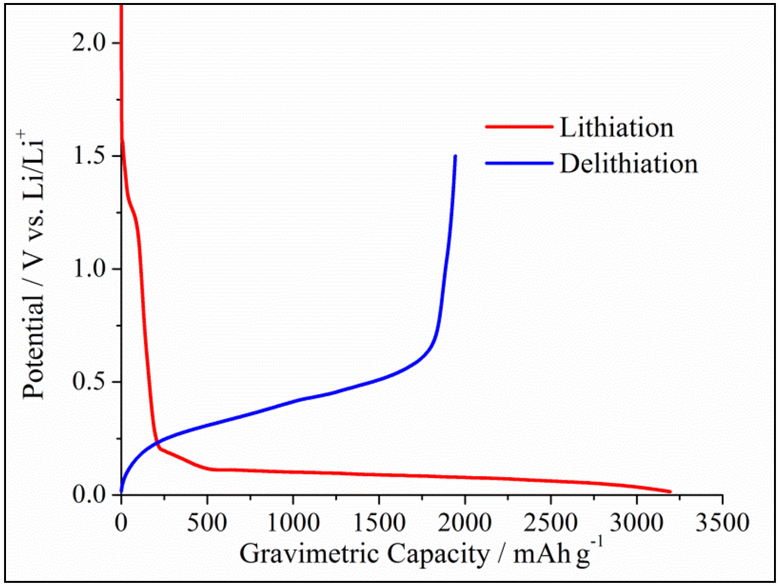
Slurry Cast Anode

- 67 wt% Si nanoparticles (50-70 nm)
- 33 wt% PFM
- 6 µm layer was cast onto Cu foil

Electrolyte Composition

- 1.2 M $LiPF_6$
- Liquid carbonates (3/7 EC/DEC w/w)
- 30 wt% FEC additive





Gravimetric capacity of Si is ~3,000 mAh/g_{Si}. Excellent stability for Si/PFM slurry cast anodes. Results are in good agreement with those reported by G. Liu at LBNL.

Electrospinning Neat PFM Fibers

Initial electrospinning experiments with PFM polymer

Solvents examined

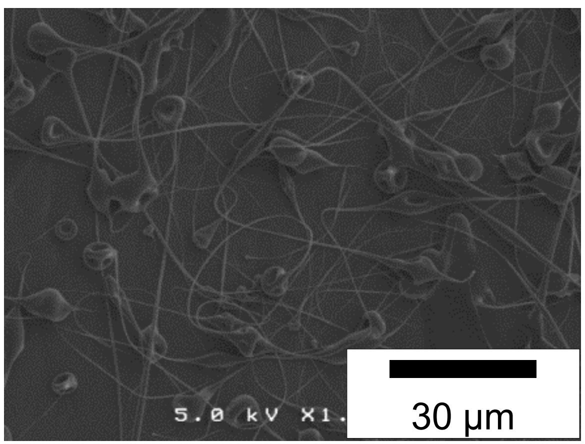
- Chloroform
- Chlorobenzene
- 1/1 chloroform/chlorobenzene (w/w)

PFM concentrations examined: 5-20 wt%

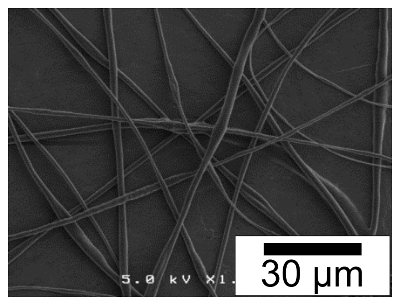
Typical electrospinning conditions:

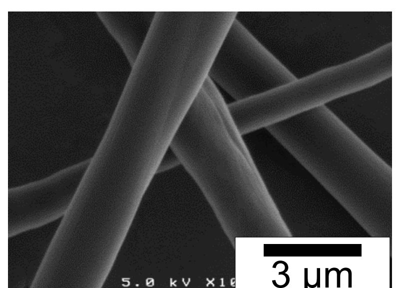
- 0.25 mL/h flow rate
- 5 kV bias voltage
- 8 cm spinneret-to-collector
- 15-75% relative humidity (RH)

Neat PFM

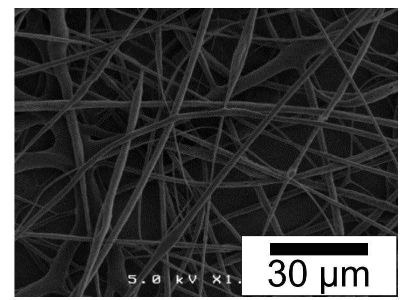


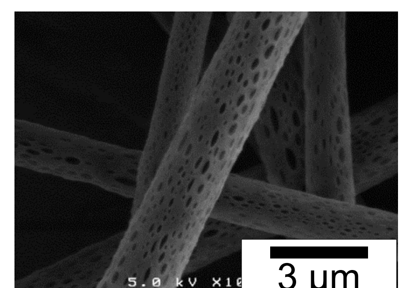
PFM/PEO (99/1)
15% RH → dense fibers
~1.5 µm diameter





PFM/PEO (99/1)
75% RH → porous fibers
~1.5 µm diameter





Addition of PEO carrier (1 wt%) allows for uniform PFM fibers. **Year 1 milestone achieved.**

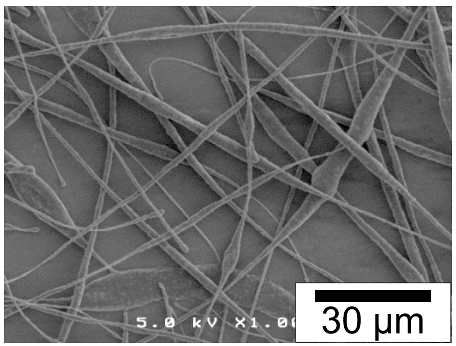
Electrospinning Fibers with Si Nanoparticles, PFM, and PEO

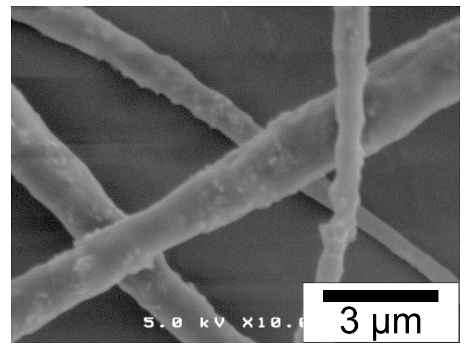
Incorporate Si nanoparticles (50-70 nm, from G. Liu) into PFM/PEO fibers

Solvent: 1/1 chlorobenzene/chloroform (w/w)

Electrospinning conditions: 0.25 mL/h, 5 kV, 8 cm, 15-75% RH

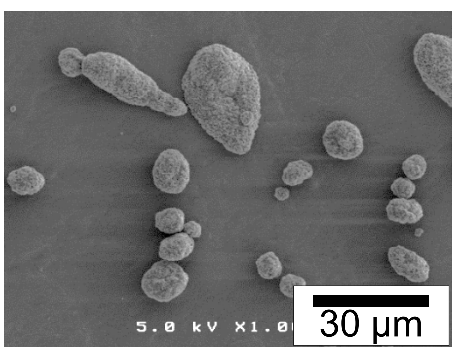
Si/PFM/PEO (20/79/1)

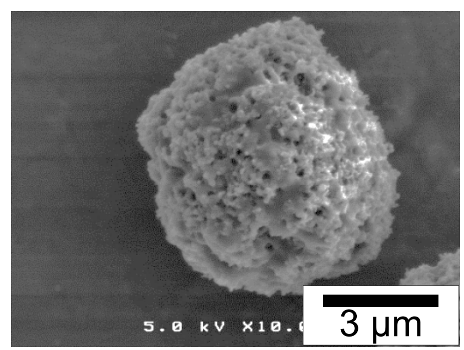




Targeted Fiber Structure

Si/PFM/PEO (67/32/1)





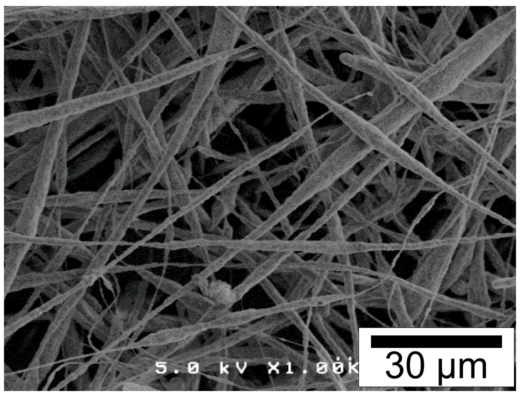
Electrosprayed Droplets

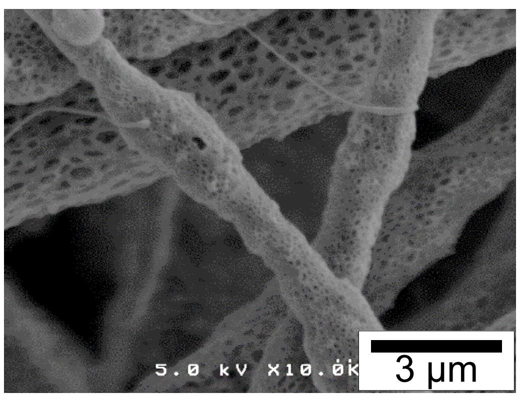
PFM/PEO fibers containing 20% Si were successfully spun. Average fiber diameter was ~1.5 µm.

Optimizing the Composition of Si/PFM/PEO Electrospun Fibers

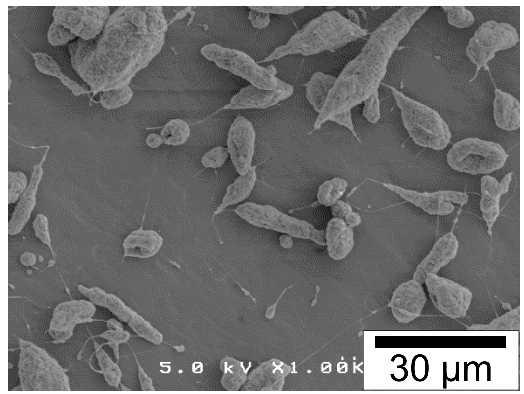
We have optimized the ink composition and spinning conditions to form fibers containing 50% Si

Si/PFM/PEO 35/64/1 – good fibers



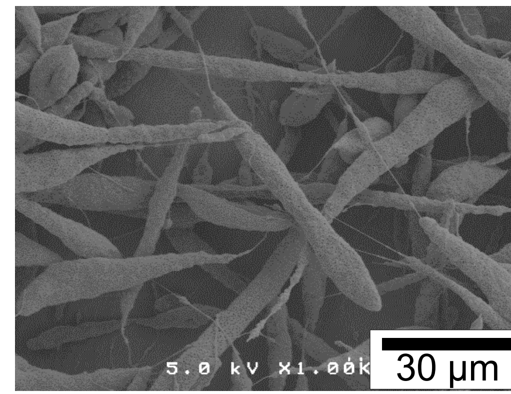


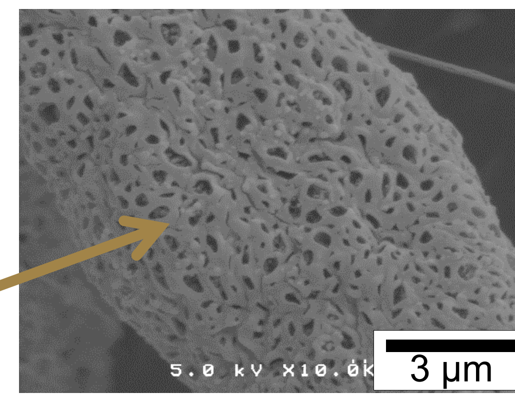
Si/PFM/PEO 50/40/10 – no fibers



9 µm fibers are porous, with 100 nm surface pores and 50 nm pore wall thickness

Si/PFM/PEO 50/49/1 – fair fiber morphology





Si/PFM/PEO fibers containing 50 wt% Si nanoparticles were successfully electrospun. The fibers have a reasonably good morphology. **Year 1 milestone achieved.**

Electrospinning Si Particles with Carbon Powder and Poly(acrylic Acid) (PAA)

Obtain preliminary data to establish baseline performance of nanofiber Si anode mats

Electrospinning ink composition:

- Si nanoparticles, carbon black, poly(acrylic acid) (PAA)
- n-propanol solvent
- 11 wt% solids (Si/C/PAA)

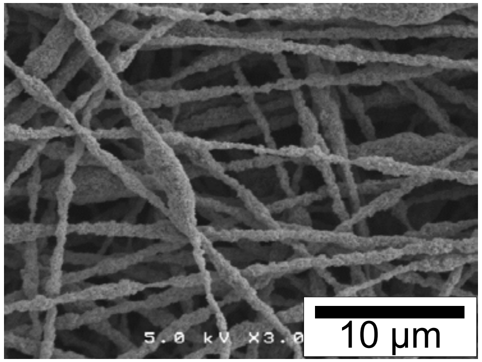
Electrospinning conditions:

- 1.00 mL/h
- 8 kV
- 8 cm spinneret-to-collector distance
- 20% RH

Electrospun Fiber Composition

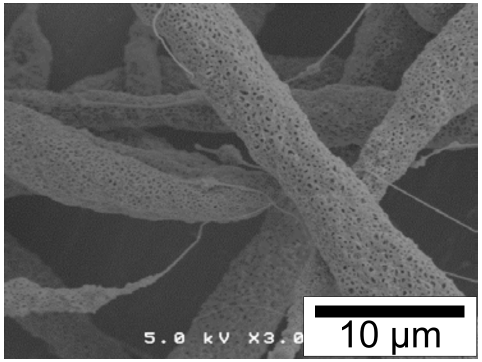
- 40 wt% Si nanoparticles
- 25 wt% carbon black
- 35 wt% poly(acrylic acid) (PAA)
- Average fiber diameter ~600 nm

Si/C/PAA Fibers (40% Si)



versus

Si/PFM/PEO Fibers (50% Si)

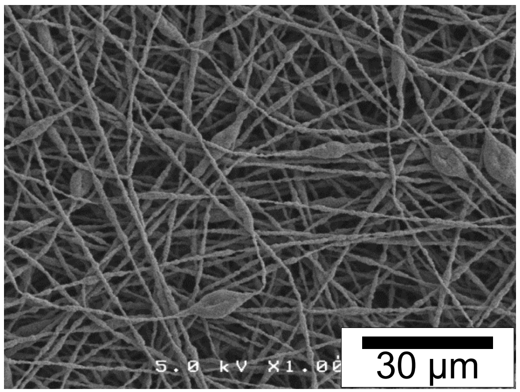


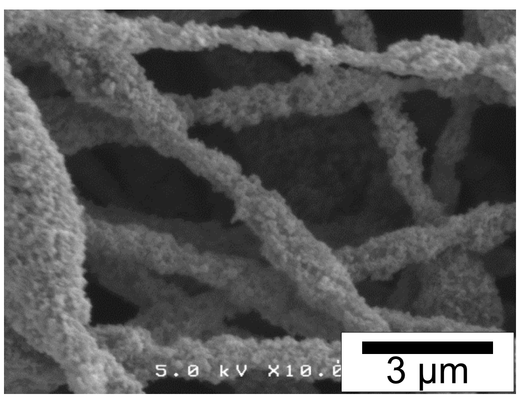
Si/C/PAA nanofibers successfully electrospun with fiber diameter ~600 nm

Si/C/PAA Fiber Mats with/without Compaction and Welding

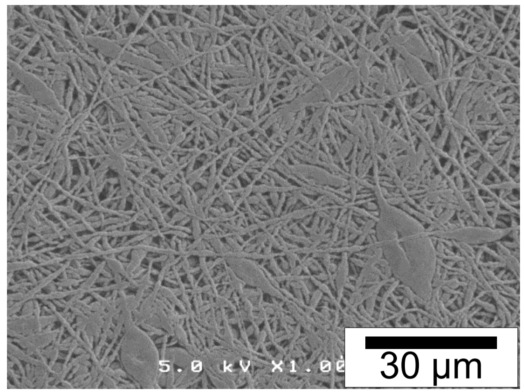
After electrospinning, compact (at 90 MPa for 40 seconds) and weld Si/C/PAA nanofibers (exposure to methanol vapor for 1 hour at RT) to improve interfiber contact.

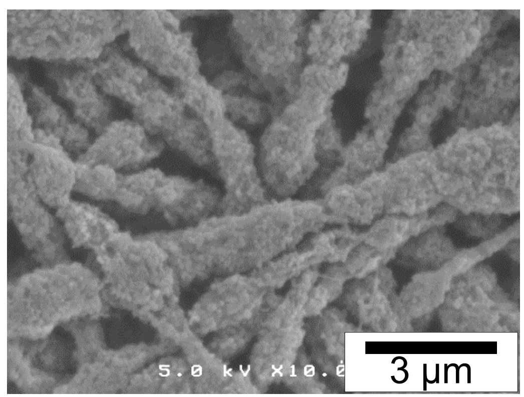
As-Spun Fibers (~25% fibers)



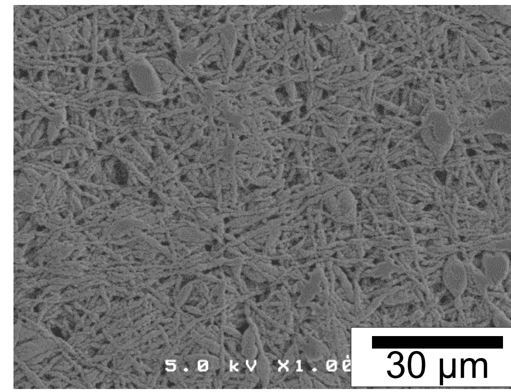


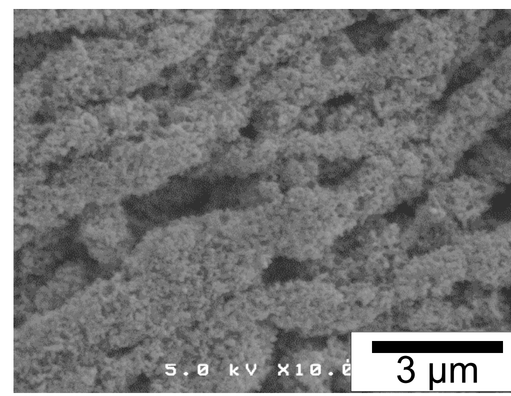
Compacted Fibers (~80% fibers)





Compacted/Welded Fibers (~80% fibers)



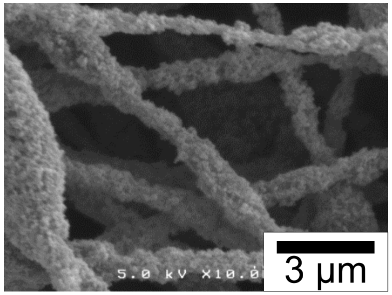


Fiber volume fractions of compacted and compacted/welded anodes are similar, but electrical resistance was reduced after welding, indicating better fiber contact.

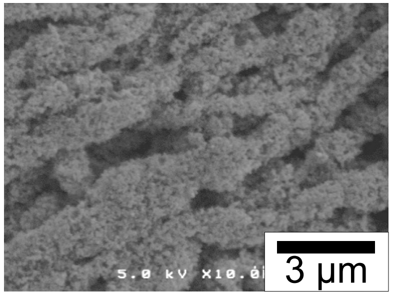
Performance of Si/C/PAA Nanofiber Mat Anodes in Half-Cell

Nanofiber anodes (40/25/35 Si/C/PAA) were tested in CR2032 half cells using a Li metal counter/reference electrode, Celgard 2500 separator, and an electrolyte containing 1.2 M $LiPF_6$ with 3/7 EC/DEC and 30% FEC additive

As-Spun Fibers

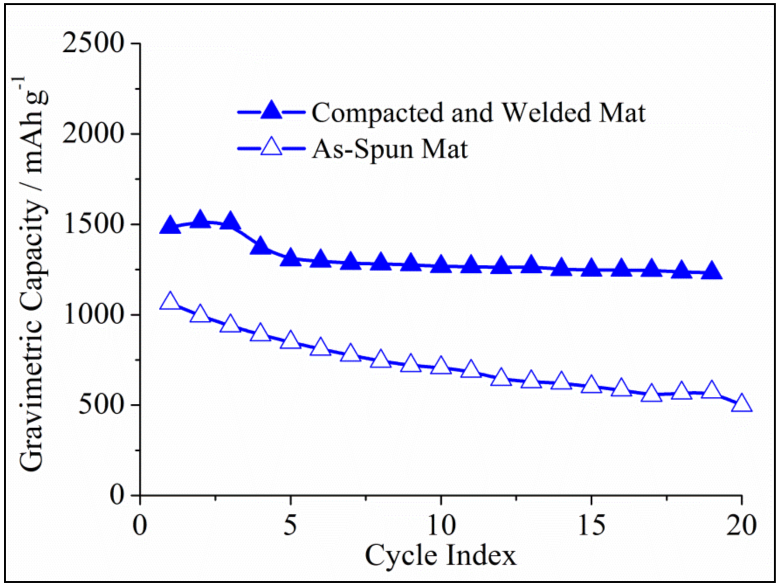


Compacted/Welded Fibers



Theoretical Gravimetric Capacity: 1,533 mAh/g

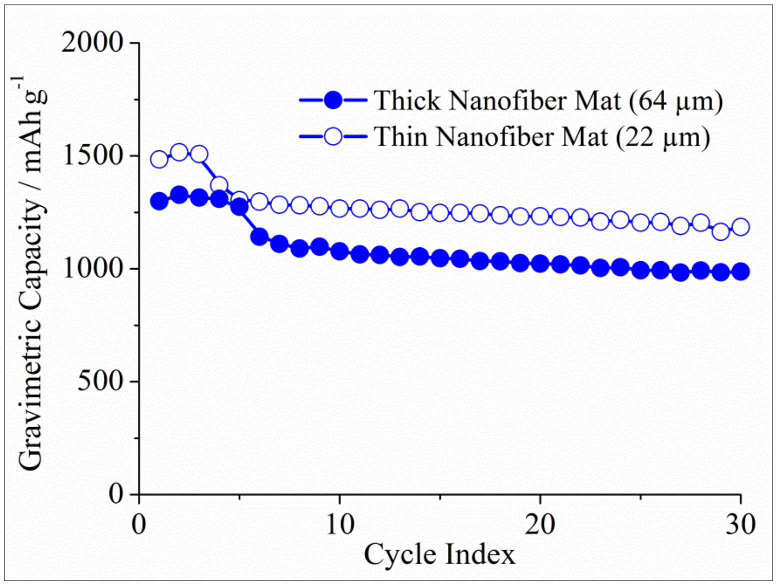
Areal Capacity: 0.9 mAh/cm^2

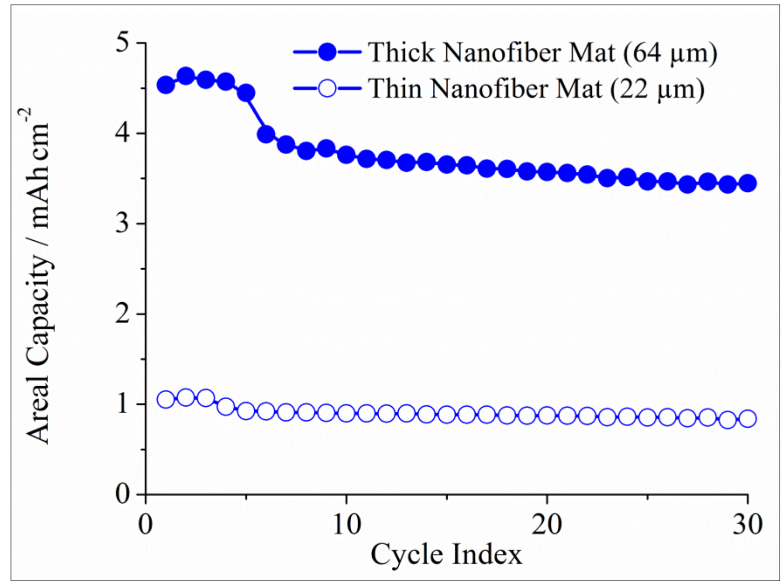


- For the as-spun mat: Initial capacity loss may be due to electrical isolation of some fibers after lithiation. Continued capacity fade with cycling is associated with isolation of more fibers during cycling.
- Compacting and welding significantly improved the mechanical strength and performance of the anode (compacting/welding is better than compaction alone and welding alone).

High Areal Capacity Si/C/PAA Nanofiber Anodes

- Compacted and welded Si/C/PAA nanofiber anode mats were prepared and tested in a half-cell.
- Performance of a thin electrode (21 μm) was compared with that of a thick electrode (62 μm)
- For the thick electrode, 5 sheets of electrospun fibers were stacked, then compacted and welded.





- Lower gravimetric capacity of the thicker electrode indicates less than 100% utilization of the Si.
- Thick electrospun Si/C/PAA nanofiber mat anodes performed very well, with a high and stable capacity over 30 cycles.
  - **A gravimetric capacity of 1,000 mAh/g and an areal capacity of 3.5 mAh/cm^2 (with a volumetric capacity of 560 mAh/cm^3)**

Response to Previous Year Reviewers' Comments

This project is a new start with no reviewer comments from the previous year

Collaborations

Partners

- **Lawrence Berkeley National Laboratory (Dr. Gao Liu):** Synthesize conductive polymer binders which are sent to Vanderbilt University for electrospinning.
- **Oak Ridge National Laboratory (Dr. Jagjit Nanda)**: Conduct electrochemical performance analysis of nanofiber anodes and provide microstructural and interfacial characterization of the electrospun materials.
- **e-Spin Technologies, Inc. (Dr. Jayesh Doshi):** Conduct preliminary scale-up of the electrospinning process at his commercial facility in year 3.

Remaining Challenges and Barriers

1. Si/PFM/PEO fiber diameter should be decreased from 9 μm to < 1 μm.

- Requires further optimization of ink composition and electrospinning conditions

2. Based on G. Liu's papers and preliminary results at Vanderbilt, slurry anodes containing PFM binder need to be < 10 μm thick for good performance.

- Problem: thin electrodes have low areal capacity (< 1 mAh/cm^2)
- Problem: low electronic conductivity of PFM binder (~$1x10^{-5}$ S/cm) will make it difficult to prepare thick (40-100 μm) nanofiber Si/PFM/PEO anodes

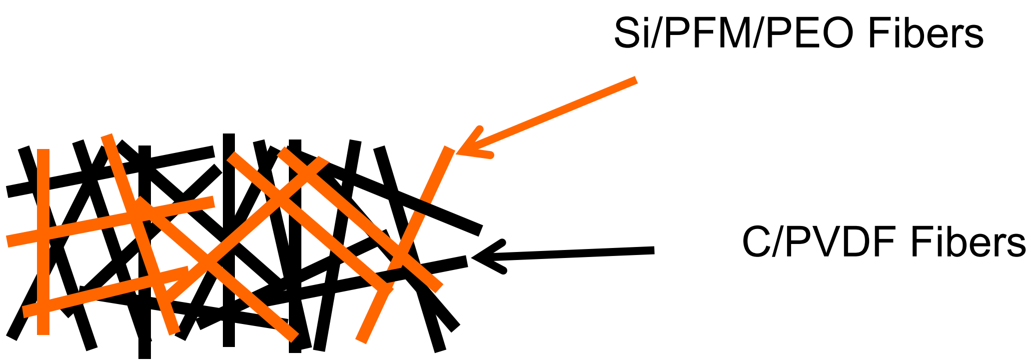
3. Need to determine how morphology (i.e., nanofiber mat vs. conventional slurry cast layer) affects electrochemical performance of Si-based anodes.

- As shown in our previous work on titania and carbon nanofiber anodes, electrospun mats contain short Li^+ transport pathways to improve rate capabilities relative to a slurry cast layer.
- Intra- and interfiber void space of a nanofiber mat can accommodate Si volumetric changes during cycling which may improve anode lifetime.
- We must determine the inter-relationship among fiber diameter, Si fiber loading (Si/binder wt. ratio), fiber volume fraction, and electrode thickness.

Proposed Future Work

1. Si/PFM/PEO nanofiber anodes
   - Continue electrospinning studies to decrease fiber diameter to <1 μm
   - Compare performance of nanofiber and slurry cast anodes in half-cells over 50 cycles at 0.1C
   - Examine Si loadings of 20-50 wt% in the fibers, with compacted and welded fiber mats

2. Dual fiber electrospinning with PFM binder
   - From G. Liu's papers and preliminary battery tests at Vanderbilt, the thickness of PFM-based slurry anodes must be ≤ 10 μm.
   - For high areal capacity (3 mAh/cm^2), electrodes 40-100 μm thick are required (depending on the Si loading and fiber volume fraction).
   - Thick electrodes can be prepared by co-spinning electrically conductive C/PVDF fibers with Si/PFM/PEO fibers.
   - 10-20 vol% conductive fibers in a Si/PFM/PEO fiber matrix may be sufficient
   - Dual fiber spinning will be carried out within the next 6 months, after collecting data on Si/PFM/PEO single fiber anodes



Summary

PFM and Si/PFM nanofiber electrospinning studies

- 1 wt% PEO is required to electrospin neat PFM and Si/PFM fibers.
- Fibers were successfully electrospun with 20 - 50 wt% Si nanoparticles with an average fiber diameter of 1.5 - 9 μm.
- Electrospinning at high RH produces fibers with surface porosity (maybe internal porosity).
- Two project milestones were met: (i) delivery of PFM polymer to Vanderbilt and (ii) electrospinning fibers with 50% Si.

Baseline half-cell data were collected on Si/C/PAA electrospun nanofiber mat anodes

- Si/C/PAA nanofibers were spun with an average fiber diameter of ~600 nm.
- Compaction and welding of fiber mats improved initial capacity and capacity retention.
- High gravimetric (1,000 mAh/g), areal (3.5 mAh/cm^2), and volumetric (560 mAh/cm^3) capacities were achieved through the use of a thick, compacted, and welded nanofiber mat anode.
- Fiber mat strength appears to be important for achieving high initial capacity and to minimize capacity fade with cycling (compaction and welding may prevent breakage and isolation of fibers during cycling).

Summary of 2015-16 Work

Relevance: Develop novel high performance Si-based anodes for Li-ion batteries.

Approach: Fabricate and characterize electrospun particle/polymer nanofiber mat Li-ion battery anodes containing Si nanoparticles and an electronically conductive binder.

Technical Accomplishments and Progress: An electronically conductive polymer binder was synthesized at LBNL and electrospun at Vanderbilt. 20 - 50 wt% Si nanoparticles were incorporated into the fibers. Fiber mats containing Si nanoparticles, carbon black, and poly(acrylic acid) binder were also prepared and characterized as a baseline system. High gravimetric, areal, and volumetric capacities were achieved for a thick (62 μm) Si/C/PAA nanofiber mat anode which was compacted and welded after electrospinning.

Collaborations: Continue collaborations with Lawrence Berkeley National Laboratory and Oak Ridge National Laboratories.

Proposed Future Research: Continue electrospinning studies for Si/PFM/PEO fibers to decrease the fiber diameter to < 1 μm. Characterize Si/PFM/PEO anodes in half-cells to achieve stable capacities > 500 mAh/g at 0.1C. Compare the performance of nanofiber and slurry cast anodes in half-cell experiments. Develop dual fiber electrospun nanofiber mats containing separate Si/PFM/PEO fibers (for Li storage) and C/PVDF fibers (for electrical conduction). Thick dual fiber mats (40-100 μm) will be prepared and tested, to achieve an areal capacity of 3 mAh/cm^2.

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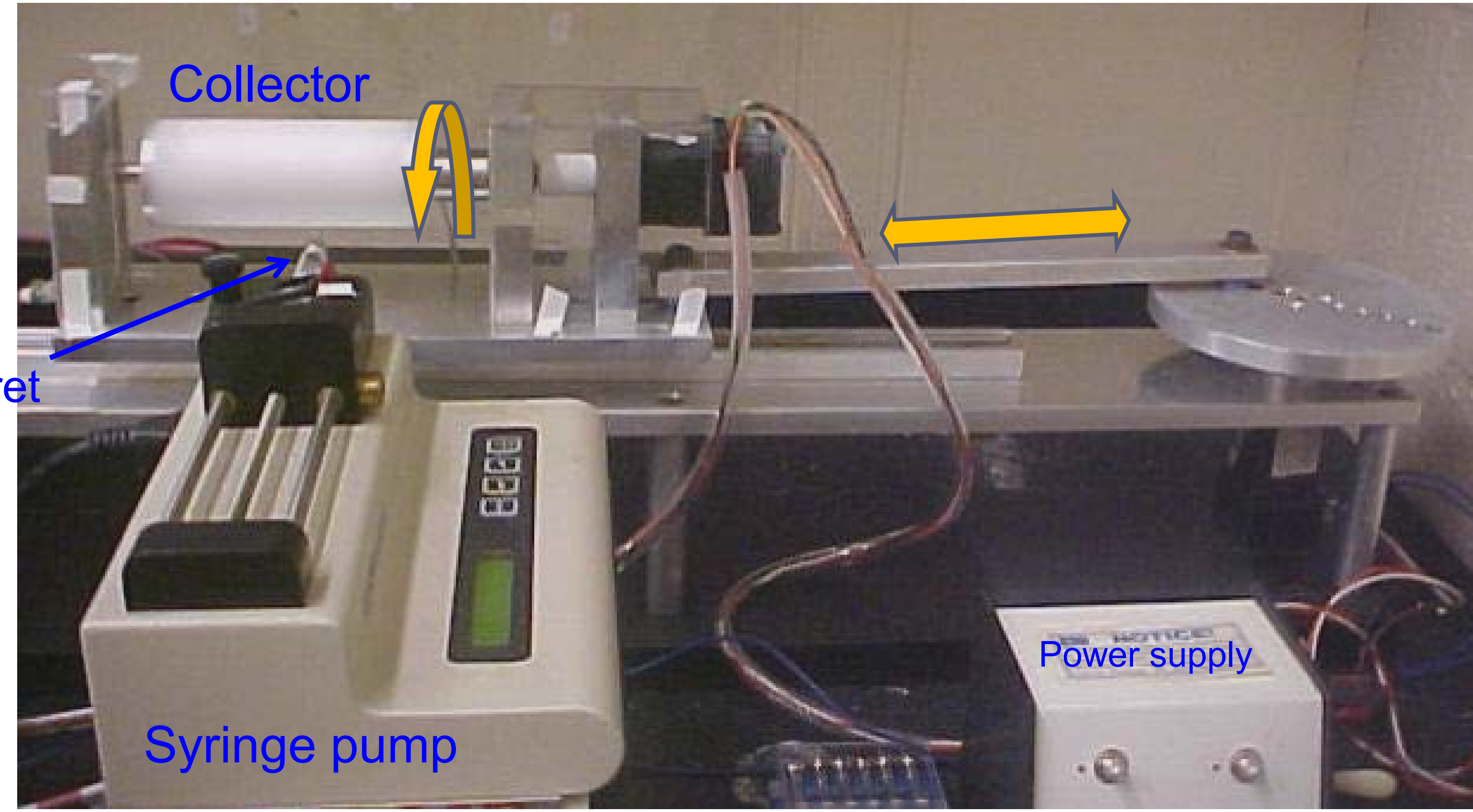
Technical Back-Up Slides

Electrospinning – Rotating Drum Apparatus



Uniform mats were made:

16 cm long, 20 cm wide and 10~120 µm thick